



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 124 194
A2

⑫

EUROPEAN PATENT APPLICATION

㉑ Application number: 84300576.0

㉓ Int. Cl.³: C 09 K 7/06, C 09 K 7/02

㉒ Date of filing: 30.01.84

㉔ Priority: 04.02.83 US 463779

㉕ Applicant: CONOCO INC., 1000 South Pine Street P.O.
Box 1267, Ponca City Oklahoma 74601 (US)

㉖ Date of publication of application: 07.11.84
Bulletin 84/45

㉗ Inventor: Boyd, Phillip A., Rt. 5, Box 70, Ponca City
Oklahoma 74601 (US)

㉘ Designated Contracting States: FR GB NL

㉙ Representative: Woodman, Derek et al, Frank B. Dehn &
Co. European Patent Attorneys Imperial
House 15-19 Kingsway, London WC2B 6UZ (GB)

㉚ Low toxicity oil-based drilling fluid.

㉛ Disclosed is a low toxicity oil for use in drilling fluids. The oil consists essentially of branched- and cyclic-paraffins, preferably having 11 to 17 carbon atoms per molecule, and further having a low aromatic content of less than about 1% and a low normal-paraffin content of less than about 5%. The low polynuclear aromatic oil is useful in both oil-based and waterbased drilling mud, particularly where low toxicity and lack of water sheen are important such as in offshore drilling environments. The oil also has the advantage of being nonfluorescent so that it does not mask UV fluorescence of formation crudes produced from the drill cuttings in wildcatting operations.

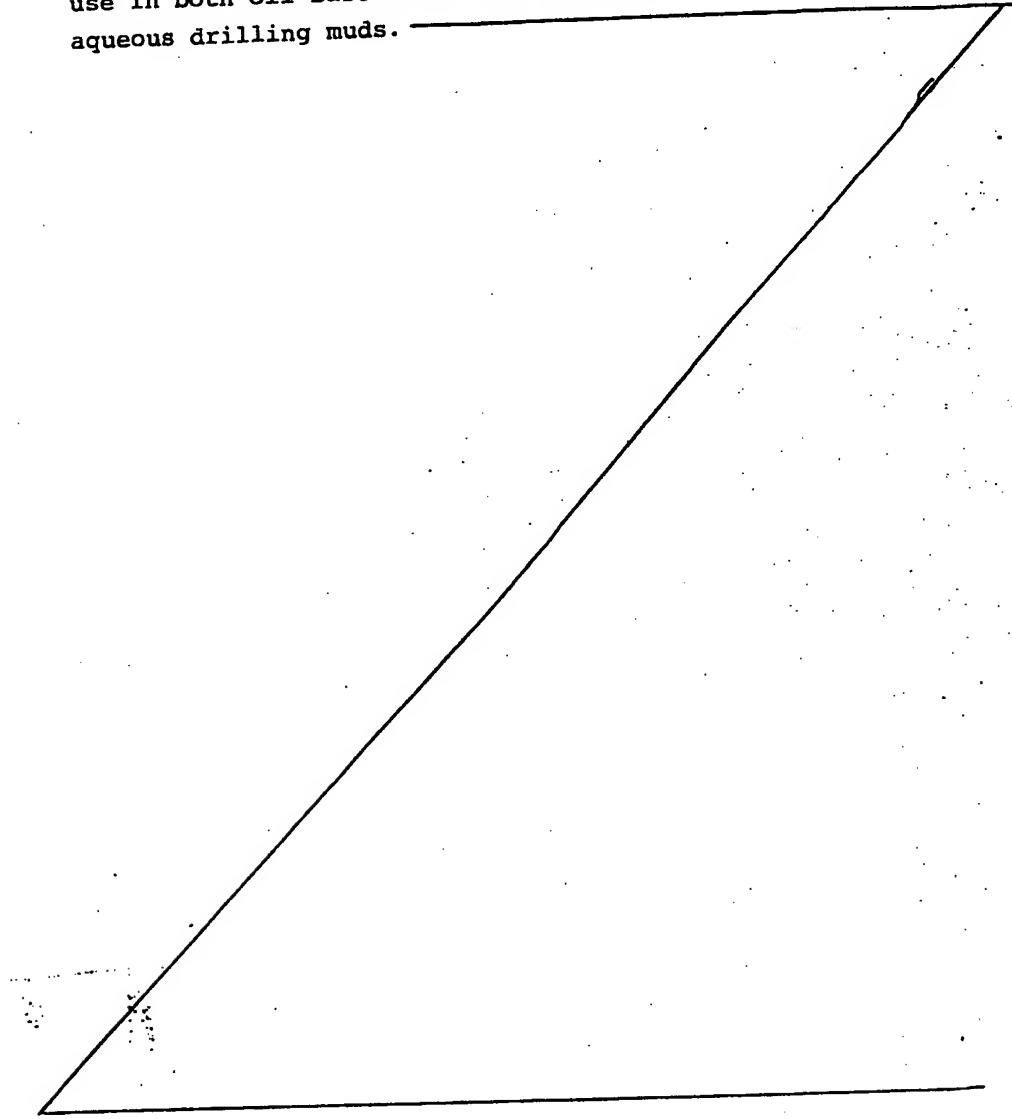
EP 0 124 194 A2

0124194

- 1 -

LOW TOXICITY OIL-BASED DRILLING FLUID

This invention relates to the art of drilling fluids and more particularly, to an improved, low toxicity oil for use in both oil-based drilling muds and as an additive to aqueous drilling muds.



-2-

Background of the Invention

It is well known that in perforating earthen formations to tap subterranean deposits such as gas or oil, the perforation is commonly accomplished by rotary well drilling tools and a drilling fluid. The drilling fluid serves to transport to the surface the material loosened by the drilling tools, such as a drill bit; to lubricate the drilling tools including the drill string thereby reducing frictional power loss; to act as a cooling fluid to absorb heat generated by the drill bit and by frictional drag of the rotating pipe; to deposit a cake or layer on the walls of the well and within the pore spaces and crevices of the wall rocks thereby sealing porous formations and reducing water loss and to seal off high pressure gas, oil or water yielding zones so that such fluids cannot enter the well bore during the drilling operation.

Both water-based and oil-based drilling fluid systems are known. The more economical water-based systems are used when practicable with oil-based systems being used where increased lubricity at the drilling head is desirable or when traversing formations which would be adversely affected by a water-based system, such as water soluble shale formations. It will be understood that while this specification refers to oil-based and water-based systems, each of these systems may contain amounts of water and oil respectively, the basing component being considered the continuous phase and generally present in an amount greater than 50% of the slurry composition. Thus, a water-based mud system would contain a greater than 50% amount of water but may also include up to 50% oil forming an oil-in-water emulsion in the mud. Similarly, an oil-based system would contain greater than 50% oil with up to 50% water being possible and forming a water-in-oil emulsion.

Oils commonly used in both oil- and water-based mud systems are commonly crude oil, diesel oil, fuel oil and the like. In U. S. Patent No. 3,668,129, preferred oils used as lubricants in aqueous drilling fluids contain some unsaturated and aromatic hydrocarbons because they facilitate blending with

-3-

other mud components. A similar preference for aromatic and unsaturated hydrocarbons is shown in U. S. Patent No. 3,948,782, 3,850,248, 3,849,316 and 3,528,914, as well as Canadian Patent No. 596,454.

5 More recently, due to the toxicity of aromatics present in these oils in amounts ranging over 25%, particularly in marine environments, paraffin-based mineral oils having an aromatic content of less than about 10% are being used. One commonly used mineral oil is sold by Exxon, Inc. under the
10 trademark Mentor-28. Such mineral oils, generally comprising normal-paraffins in the C₁₁ to C₂₀ range of carbon chain length, are finding favor for use in oil-based drilling muds used in off-shore drilling operations where toxicity to marine life is an important environmental consideration.

15 In addition to the toxicity problems, Coast Guard and Environmental Protection Agency regulations require that there be no discharge from any marine drilling operations which causes a sheen, film or discoloration to form on the water surface. All of the above-mentioned oils would create a water
20 surface sheen upon discharge from drilling operations. Thus, overboard discharge of drill cuttings produced during drilling operations using an oil-based mud with any of the above-mentioned oils would be prohibited without some sort of washing treatment prior to discharge. Otherwise, such cuttings would need to be
25 accumulated and hauled to shore for treatment and/or disposal. The washing of drill cuttings requires extra equipment which raises the cost of a drilling rig while further increasing the cost of an offshore platform due to the need for additional deck space and weight capacity for such equipment. Carry off
30 disposal is also a costly operation.

Another problem with the use of oils having a high aromatic and olefin content has been recognized by Canadian Patent No. 649,477. In drilling so-called "wildcat" exploratory wells, it is common to use a water-based drilling mud so that
35 cuttings and/or core sections may be inspected for UV fluorescence which indicates the presence of crude oil in the formation being traversed. Since all of the above-mentioned oils for use in drilling fluids are high in aromatics and unsaturates which

would cause such fluorescence, the use of an oil-based drilling mud precludes the use of this valuable exploratory technique.

In the afore-mentioned Canadian Patent No. 649,477, the patentee provides for an oil-in-water emulsion for use as an oil-based

5 drilling fluid which limits the aromatics and unsaturates in the oil and any emulsifier used to a level of 5% or less.

The refined oil is subjected to Edeleanu (SO_2 liquid in benzene) processing followed by clay treatment to remove aromatics and unsaturates. A "thermally stable" oil which evidences no

10 appreciable discoloration upon heating to at least 250°F is produced.

Summary of the Invention

The present invention provides an improved oil for use in both oil-in-water based drilling fluids which oil has low toxicity with respect to the marine environment, which creates no film, sheen or discoloration to the water surface upon discharge and which does not fluoresce when present in drill cuttings.

In accordance with the invention, a low polynuclear aromatic oil for use in drilling fluids consists essentially of a mixture of branched- and cyclic-paraffins (preferably C_{11} to C_{17} branched- and cyclic-paraffins) having an aromatic content of less than about 1% and a normal-paraffin content of less than about 5%. In its most preferred form, the oil of this invention contains less than about 0.5% aromatics and less than about 1% normal-paraffins.

Further in accordance with the invention, a low toxicity, oil-based drilling mud comprises greater than 50% of the above-described low toxicity, low polynuclear aromatic oil, less than 50% water, and various mud components such as emulsifiers, alkalinity control agents, viscosifiers, filtration control reagents, weighting agents, brine and wetting agents.

Still further in accordance with the invention, a water-based drilling fluid comprises greater than 50% water and less than 50% of the above-described low polynuclear aromatic oil in a mud system which further includes normal mud additives such as emulsifiers, alkalinity control agents, viscosifiers, filtration control reagents, weighting agents, brine and wetting agents.

Still further in accordance with the invention, a method of drilling a borehole comprises injecting a drilling mud

-5-

into the area adjacent the drill bit of a rotary drill string,
the drilling mud consisting essentially of a low toxicity, low
polynuclear aromatic oil having less than about 1% aromatic
content and less than about 5% normal paraffin content, the oil
5 preferably being characterized as a mixture of branched- and cyclic-
paraffins having 11 to 17 carbon atoms per molecule of branched-
and cyclic-paraffin; water and common drilling fluid additives
which are known in the art.

It is therefore an object of this invention to provide
15 a low toxicity oil-based drilling fluid which can be used in
the marine environment without the need for treatment of drill
cuttings prior to discharge so that a prohibited sheen on the
water surface may be avoided.

It is another object of this invention to provide an
15 oil which may be used in water-in-oil based drilling mud system
which avoids the problems of toxicity and sheen associated with
the use of prior oils employed in such drilling fluids.

It is a further object of this invention to provide a
20 oil-based drilling mud which does not mask an indication of the
penetration of a hydrocarbon-bearing formation by fluorescence
of the drilling mud cuttings stream returned from the borehole.

Detailed Description of the Preferred Embodiments

These and other objects of the invention are accom-
plished through the manner and form of the present invention
25 to be described hereinafter in the more limited aspects of a
preferred embodiment thereof. It will be understood by those
skilled in the art that such a detailed description including
specific examples of the invention in the form of preferred
embodiments thereof do not constitute a limitation on the broader
30 application of the invention as a whole.

A by-product stream from refining operations conducted
by the assignee of this invention comprises a low polynuclear
aromatic, high purity aliphatic hydrocarbon having a molecular
weight range similar to kerosine. It is a colorless liquid having
35 a mild odor, low viscosity and extremely low aromatic, olefinic
and normal-paraffinic content. The material, known as CONOCO®
LPA Solvent, results from a refining process in which kerosine
distillate is passed through a molecular sieve to remove the normal-
paraffins therein for other desired purposes. The remaining
40 material having a very low normal-paraffin content comprises

-6-

complex aromatic and olefinic hydrocarbons. This mixture is then catalytically hydrogenated to produce the desired solvent material which is generally 95 to 99% branched- and cyclic-paraffins. The material has a normal-paraffin content of less than 5% and preferably less than 1% and an aromatic content which is less than 1% and preferably less than 0.5%. The solvent material qualifies under 21 CFR as a "odorless light petroleum hydrocarbon" which may be used as both "food additives permitted in food for human consumption" as well as "indirect food additives".

A typical gas chromatography-mass spectroscopy analysis of the oil is set forth in Table I.

0124194

-7-

	<u>Component</u>	<u>TABLE I</u>	<u>% Total</u>
	Decane		0.01
	Undecane		0.02
5	Dodecane	<u>0.16</u>	0.03
	Tridecane		0.05
	Tetradecane		0.04
	Pentadecane		0.01
	Hexadecane		0.01
10	Branched C-10 Paraffins		3.8
	Branched C-11 Paraffins		3.8
	Branched C-12 Paraffins		5.1
	Branched C-13 Paraffins		5.2
	Branched C-14 and C-15 Paraffins	<u>31</u>	8.9
15	Branched C-15 and C-16 Paraffins		2.8
	Branched C-16 and C-17 Paraffins		1.1
	Branched C-17 and C-18 Paraffins		0.01
	C-9 Cycloparaffins		4.1
	C-10 Cycloparaffins		5.2
20	C-11 Cycloparaffins		8.3
	C-12 Cycloparaffins	<u>22</u>	2.5
	C-13 Cycloparaffins		1.5
	C-14 Cycloparaffins		0.61
	C-15 Cycloparaffins		0.01
25	C-9 Dicycloparaffins		0.02
	C-10 Dicycloparaffins		4.0
	C-11 Dicycloparaffins	<u>45</u>	19
	C-12 Dicycloparaffins		15
	C-13 Dicycloparaffins		5.3
30	C-14 Dicycloparaffins		1.3
	C-15 Dicycloparaffins		0.07
	C-11 Tricycloparaffins		0.94
	C-12 Tricycloparaffins		0.88
	C-13 Tricycloparaffins	<u>3.0</u>	0.80
35	C-14 Tricycloparaffins		0.35
	C-12 Tetracycloparaffins		0.03
	C-13 Tetracycloparaffins	<u>0.08</u>	0.04
	C-14 Tetracycloparaffins		0.01
	C-5 Benzenes		0.01
40	C-6 Benzenes	<u>0.04</u>	0.01
	C-7 Benzenes		0.03
	AVERAGE CARBON NUMBER		<u>11.9</u>

The low polynuclear aromatic oil is further defined as having a distillation range of 350°F to 530°F (177°C to 277°C); a Pensky-Martens flash point ranging from a minimum of 140°F (65°C) up to 180°F (82°C); a specific gravity of about 0.8; 5 an aniline point greater than 160°F (71°C) and a Kauri-butanol value of about 31.5.

In accordance with the present invention, it has been found that this by-product oil may be substituted for commonly used oil basing materials in drilling muds. It has further 10 been found that the toxicity of the drilling mud is significantly lowered when compared to drilling muds employing prior oil additives such as crude oil, fuel oil and diesel oil. The following examples will serve to illustrate the effectiveness of the low polynuclear aromatic, branched- and cyclic-paraffin oil of this 15 invention in drilling mud formulations as compared to formulations utilizing prior known oil basing fluids. Examples are also presented which show a favorable comparison between the toxicity of prior oil basing fluids and the low polynuclear aromatic, cyclic- and branched-paraffin oil of this invention.

20

Example 1

A 70/30 oil to water ratio controlled filtrate drilling fluid having a density of about 12.0 lbs per gallon was formulated utilizing LPA Solvent and with No. 2 diesel. The two formulations were as set forth in Table II as follows:

25

TABLE II

	<u>LPA System Formulation</u>	<u>Diesel System Formulation</u>	
	LPA Solvent (bbl)	0.57	#2 Diesel Oil (bbl)
	Kenol-ES (lbs)	8	Kenol-Concentrate (lbs)
	Kenox (lbs)	4	Kenox (lbs)
30	Ken-Gel (lbs)	3.6	Ken-Gel (lbs)
	VR (lbs)	8	VR (lbs)
	30% CaCl ₂ Brine (bbl)	0.26	30% CaCl ₂ Brine (bbl)
	Kencal-L (lbs)	4	Kencal-L (lbs)
35	Barite (lbs)	208	Barite (lbs)
			216

0124194

-9-

Kenol-ES, Kencal-L, Ken-Gel, and VR are trademarks of IMCO for a primary emulsifier (fatty acid blend), secondary emulsifier (oil wetting surfactant), viscosifier (organophilic clay) and filtration control reagent (organophilic lignite),
5 respectively.

It should be noted that additional amounts of organophilic clay viscosifier were required to achieve proper rheology for the LPA solvent system. This is believed to be a consequence of its low aromatic content as compared with Diesel fuel.

10 Following mixing for 90 minutes and hot rolling at 200°F for a period of sixteen hours to simulate downhole use and circulation, the rheology and emulsion stability of each of the muds was tested at 120°F. The test results reported in Table III show similar performance between the mud formulated with No. 2 Diesel
15 and that formulated with the low polynuclear aromatic, branched-and cyclic-aliphatic oil blend of this invention.

TABLE III

		<u>LPA System</u>	<u>Diesel System</u>
20	Plastic Viscosity (PV) (centipoise)	27	30
	Yield Point (YP) (lbs/100 ft ²)	8	6
	Gel-Strengths ₂ , (10 sec and 10-min) (lbs/100 ft ²)	4/7	3/7
25	Emulsion Stability (ES) (Volts)	670	440
	High-Temperature-High-Pressure Filtrate (HTHP) (300°F, 500 psi) ml	4.8 all oil	5.2 all oil
30	Solids Settling	None	None
	Mud Weight (ppg)	12.0	12.0
	Oil/Water Ratio	70/30	70/30

0124194

-10-

Example 2

An 80/20 oil-to-water ratio relaxed-filtrate 12.0
 lbs/gal mud system was formulated using LPA Solvent and #2 Diesel
 in a manner similar to the above. The formulations were as set
 forth in Table IV.

TABLE IV

<u>LPA System Formulation</u>		<u>Diesel System Formulation</u>	
LPA Solvent (bbl)	0.62	#2 Diesel Oil (bbl)	0.64
Kencal-L (lbs)	6.4	Kencal-L (lbs)	6.4
30% CaCl ₂ Brine (bbl)	0.17	30% CaCl ₂ Brine (bbl)	0.16
Ken-Gel (lbs)	5.2	Ken-Gel (lbs)	1.0
Barite (lbs)	224	Barite (lbs)	230
Mixing Time (min)	90		90

Following mixing for 90 minutes and hot rolling at
 15 200°F for sixteen hours the rheology and emulsion stability of
 the muds were tested at 120°F, the tests showing good agreement
 in the performance between the two base oils as illustrated in
 Table V.

TABLE V

	<u>LPA System</u>	<u>Diesel System</u>
Plastic Viscosity (PV) (centipoise)	18	14
Yield Point (YP) (lbs/100 ft ²)	4	5
Gel-Strengths ₂ (10-sec and 10-min) (lbs/100 ft ²)	4/8	3/4
Emulsion Stability (ES) (volts)	980	1040
High Temperature, High Pressure Filtrate (HTHP) (300°F, 500 psi) ml	11.6 all oil	17 all oil
Solids Settling	None	None
Mud Weight	12.0	12.0
Oil/water ratio	80/20	80/20

-11-

Toxicity of #2 Diesel fuel to marine life is an important consideration in the selection of a base oil for use in drilling muds offshore. A test was made to compare the toxicity of muds formulated with the low polynuclear aromatic oil of this invention with that of #2 Diesel fuel as set forth in Examples 3 and 4 below.

Example 3

In order to obtain the water soluble fraction of each material, one part oil was added to nine parts artificial seawater in glass containers. The mixture was slowly stirred for 20 hours and the oil and water phases were separated by siphoning. Toxicity tests were conducted according to the basic procedures identified in Section F of the U. S. Environmental Protection Agency Procedures Manual entitled "Bioassay Procedures for the Ocean Disposal Permit Program" (U.S. EPA, 1978). Mysid shrimp (Mysidopsis bahia) employed as test organisms were all less than 6 days old. Artificial seawater was used to dilute the water phase of each mixture to appropriate test concentrations and as the control. Aeration was not needed to maintain levels of dissolved oxygen in test media above 4 ppm. Three replicates of each tested material were made.

Results of the toxicity tests are reported as parts per million of the water phase containing the water soluble fraction of each test material. Test results were interpreted by standard statistical techniques. The moving average method was employed to calculate 24-, 48-, and 96-hour LC 50 in each case. The 48-hour and 96-hour LC 50 for Mysid shrimp exposed to the water phase containing the water soluble fraction of the low polynuclear aromatic oil of this invention was 1,000,000 ppm.

The 48-hour and 96-hour LC 50 for Mysid shrimp exposed to the water phase containing the water soluble fraction of Mentor 28 mineral oil was similarly 1,000,000 ppm.

The 48-hour LC 50 for Mysid shrimp exposed to the water phase containing the water soluble fraction of #2 Diesel fuel was 258,600 ppm (0.95 confidence interval = 144,600 to 371,600). The 96-hour LC 50 was 70,700 ppm (0.95 confidence interval = 55,200 to 88,600).

The LC 50 tests measure the concentration of the tested material in which at least a 50 percent survival rate for the

0124194

-12-

shrimp is achieved. In the above tests, 90% of the shrimp in the control sample containing only artificial seawater survived. In the tests of LPA solvent and Mentor 28 oil, 100% concentration of the water phase solution resulted in 90% survival in the LPA (equal to the control) and 75% survival in the Mentor 28. Thus, in summation, it can be seen that the water soluble portion of LPA solvent is substantially non-toxic to marine life, Mentor 28 oil is slightly toxic, while #2 Diesel fuel is moderately toxic.

10 Example 4

This example compares the acute toxicity of drill cuttings which have been soaked in laboratory prepared LPA solvent-based drilling mud; laboratory prepared and field-collected #2 Diesel oil-based drilling mud, and cuttings which have been washed following soaking in a field-collected #2 Diesel oil-based drilling mud.

Toxicity tests were conducted according to the basic procedures identified in Annexes I and III of the protocols developed by Region II, U. S. Environmental Protection Agency and the Offshore Operators Committee (1980). The solid phase bioassays were performed with sand shrimp (Crangon septemspinosa), hard clams (Mercenaria mercenaria), and sandworms (Nereis virens). All species were tested in the same 38-liter (10-gallon) aquaria at 20 \pm 1°C in artificial seawater with a control subtidal zone sea sediment consisting primarily of sand. Table VI summarizes the data produced by solid-phase bioassays with sand shrimp, hard clams and sandworms.

TABLE VI

	<u>Cuttings</u>	<u>Percent Survival</u>		
		<u>Sand Shrimp</u>	<u>Hard Clams</u>	<u>Sandworms</u>
30	Control (no cuttings)	98	98	96
	LPA Mud Treated cuttings (Lab)	12	98	99
35	Diesel Mud Treated cuttings (Lab)	0	68	0
	Diesel Mud Treated cuttings (Field)	0	99	69
	Washed Diesel Mud Treated Cuttings	0	99	100

0124194

-13-

Sand shrimp were extremely sensitive to all types of
mud treated drill cuttings (survival range from 0 to 12%). Only LPA solvent
day exposure. In addition, the toxicity of all shrimp to survive the 10
hours of exposure. Unwashed field sample diesel drill cuttings killed within 48
reduced worm survival by 31%, laboratory sample diesel drill cuttings
cuttings killed all worms and washed diesel drill cuttings and
10 LPA drill cuttings did not reduce survival below the control
level. Hard clams were apparently unaffected by any of the
cuttings except for a 32% reduction in the survival of worms.
15 invention as a base oil fluid for oil based drilling muds offers
a further advantage of using an oil-based drilling mud without
masking the fluorescence which provides a driller with an early
indication of a hydrocarbon formation being entered by the drill
string during drilling. The presence of crude in the drilling
mud utilizing the low polynuclear aromatic oil of this
20 can be easily detected by fluorescence of the mud without
violet light stimulation. Since diesel oil and other lower
toxicity normal-paraffin based oils fluoresce under these condi-
tions, the use of LPA solvent as an oil base (which does not
25 fluoresce) allows the driller or explorationist an indication
of subsurface hydrocarbons present in the earthen formation
being drilled.
From the foregoing it can be seen that the present
invention provides an improved oil for use in both oil-in-water
based drilling fluids which has low toxicity with respect to
the marine environment. It has also been shown that discharge
30 of drilling materials containing the low polynuclear aromatic
oil of this invention would create no apparent film, sheen or
discoloration to the water surface. Further, no fluorescence is
indicated in drill cuttings by the use of the low polynuclear
aromatic oil of this invention offering the explorationist the
35 advantage of an early indication of a hydrocarbon bearing forma-
tion being traversed by the drilling operation.

0124194

-14-

It has further been shown that in accordance with the invention, a low polynuclear aromatic oil of low toxicity for use in drilling fluids comprises a mixture of C₁₁ to C₁₇ branched- and cyclic-paraffins having an aromatic content of less than 5 about 1% and a normal-paraffin content of less than about 5%.

While the invention has been described in the more limited aspects of a preferred embodiment thereof, other embodiments have been suggested and still others will occur to those skilled in the art upon the reading and understanding of 10 the foregoing specification. It is intended that all such embodiments be included within the scope of this invention as limited only by the appended claims.

Claims

1. A drilling fluid for use in rotary drilling of earthen formations consisting essentially of a low polynuclear aromatic, branched- and cyclic-paraffin oil having an aromatic content of less than about 1% and a normal-paraffin content of less than about 5%.
2. A drilling fluid as claimed in claim 1 wherein the drilling fluid is an oil-in-water emulsion containing less than 50% by volume of said low polynuclear aromatic, branched- and cyclic-paraffin oil.
3. A drilling fluid as claimed in claim 1 wherein the drilling fluid is a water-in-oil emulsion containing greater than 50% by volume of said low polynuclear aromatic, branched- and cyclic-paraffin oil.
4. A drilling fluid as claimed in any one of the preceding claims further including at least one drilling fluid additive selected from the group consisting of emulsifiers, viscosifiers, alkalinity control agents, filtration control reagents, weighting agents, brine, and wetting agents.
5. A drilling fluid as claimed in any one of the preceding claims wherein said low polynuclear aromatic oil consists essentially of 95 to 99% by weight branched- and cyclic-paraffins having 11 to 17 carbon atoms per molecule.
6. A drilling fluid as claimed in any one of the preceding claims wherein said low polynuclear aromatic oil contains less than about 0.5% by weight aromatic hydrocarbons.
7. A drilling fluid as claimed in any one of the preceding claims wherein said low polynuclear aromatic oil has a normal-paraffin content of less than about 1% by weight.
8. A method of drilling a borehole comprising the steps of: providing a rotary drilling rig having a rotating drill bit in the borehole; and injecting into the borehole at the rotating bit a drilling fluid as claimed in any one of the preceding claims.
9. A method as claimed in claim 8 further including the steps

0124194

-16-

of collecting drill cuttings produced by the rotating drill bit and inspecting the collected drill cuttings under ultraviolet light in order to note fluorescence thereof.